Supporting Information for:

Oxidative Addition of Iodomethane to Charge-tuned Rh^{I} Complexes.

*Massimiliano Delferro, Matteo Tegoni, Vincenzo Verdolino, Daniele Cauzzi,**

Claudia Graiff and Antonio Tiripicchio

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Viale G. P. Usberti 17/A, I-43100, Parma, Italy.

Tel. +390521905467; Fax +390521905557

E-mail: cauzzi@unipr.it

Table S1. Mulliken populations in gas phase and solution (PCM, CH_2Cl_2) for **1**, **2** and **3**. Only the relevant atoms are reported. For compound **2**, the protonation is on the atom N1 [B3LYP/BS-I//B3LYP/BS-I; BS-I = 6-31g** + DGDZVP (Rh)]

					Gas					
	Rh	**S1**	**S2**	**N1**	**N2**	**N3**	**P1**	**P2**	**C**	**O**
1	-0,217	-0,093	-0,093	-0,382	-0,382	-0,833	0,926	0,926	0,341	-0,289
2	-0,191	0,062	-0,039	-0,413	-0,355	-0,838	0,897	0,925	0,340	-0,249
3	-0,151	0,101	0,101	-0,406	-0,406	-0,846	0,894	0,894	0,335	-0,215
					CH_2Cl_2					
	Rh	**S1**	**S2**	**N1**	**N2**	**N3**	**P1**	**P2**	**C**	**O**
1	-0,229	-0,164	-0,165	-0,364	-0,364	-0,858	0,927	0,927	0,347	-0,327
2	-0,193	0,046	-0,112	-0,408	-0,360	-0,861	0,896	0,926	0,343	-0,295
3	-0,158	0,079	0,078	-0,401	-0,406	-0,862	0,896	0,896	0,338	-0,264

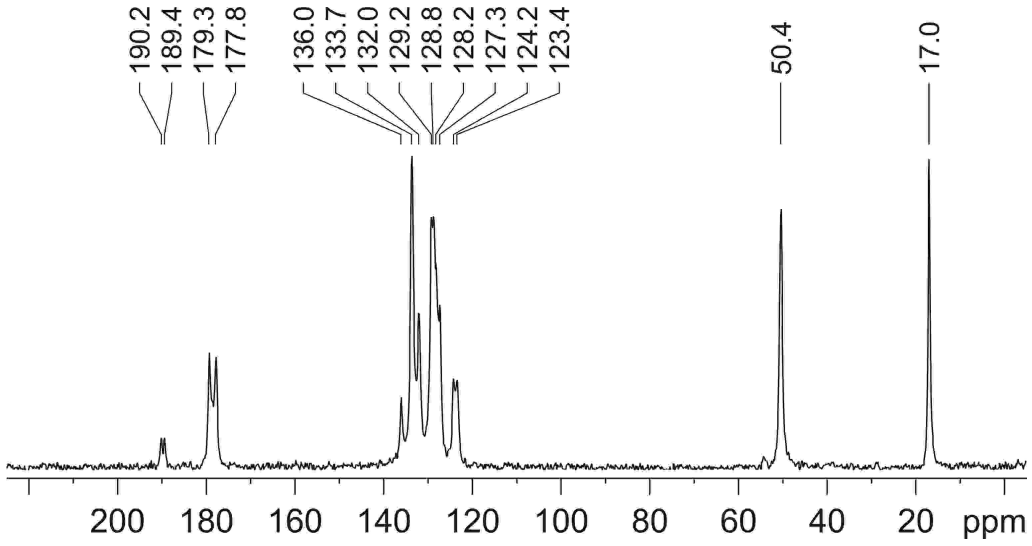

Figure S1. CP-MAS ^{13}C NMR of **1**.

CP-MAS ^{13}C NMR: δ = 189.8 (d, $^{1}J_{C,Rh}$ = 80.5 Hz, CO), 178.5 (d, $^{1}J_{C,P}$ = 151 Hz, C=N), 136.0-123.4 (m, Ph), 50.4 (s, -$CH_2$$CH_3$), 17.0 (s, -$CH_2$$CH_3$) ppm.

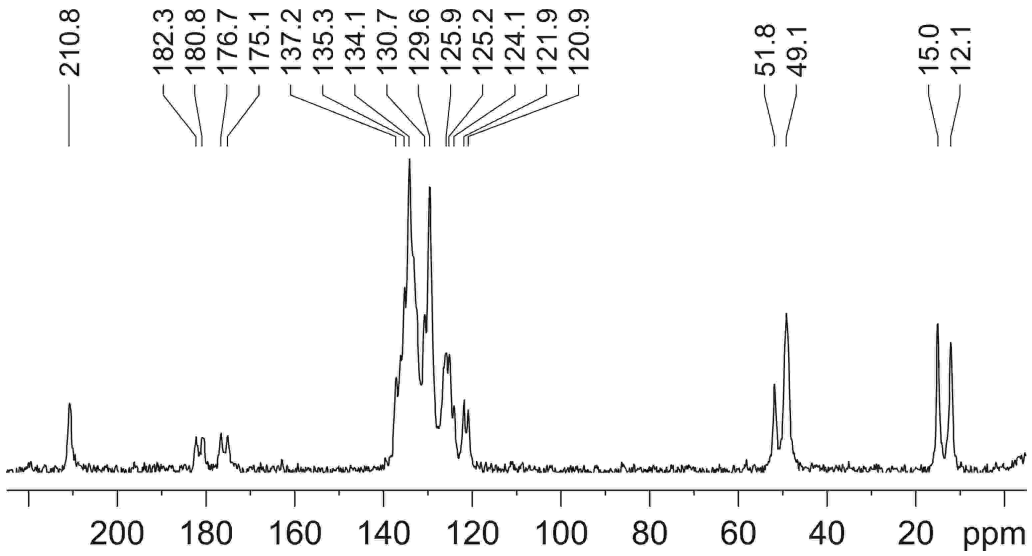

Figure S2. CP-MAS ^{13}C NMR of **4**.

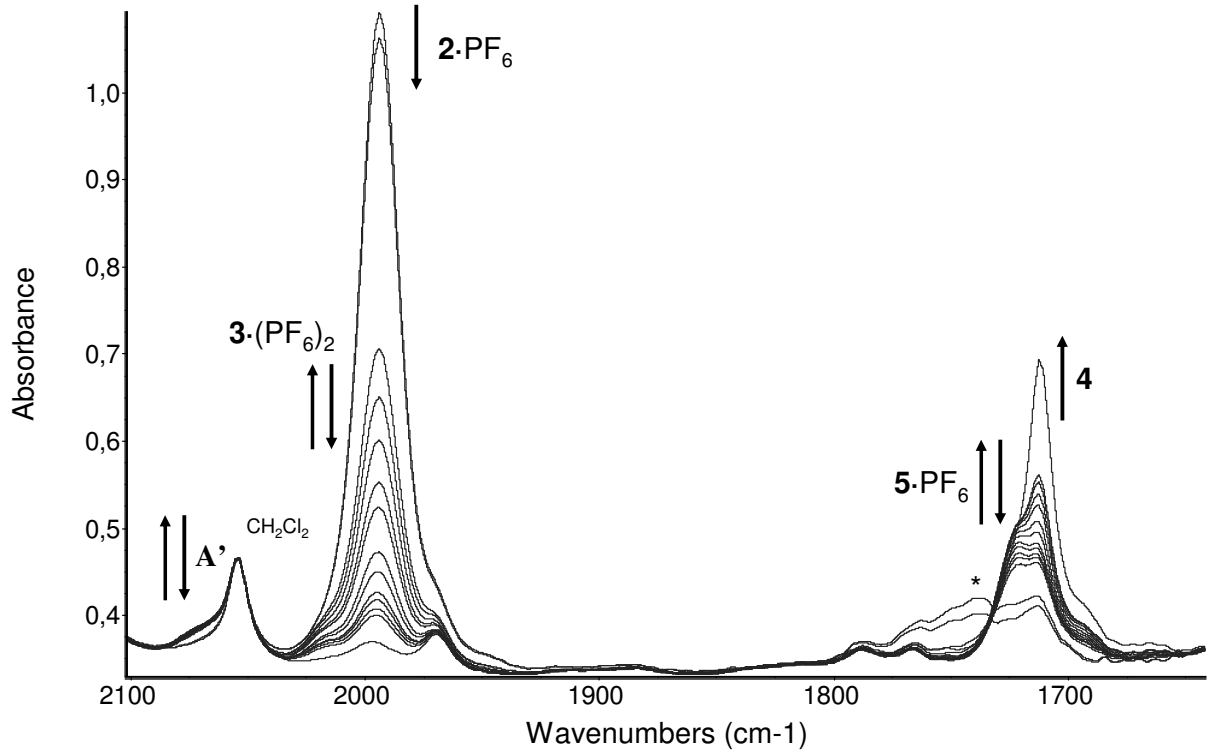

Figure S3. Superimposed FTIR spectra in CH_2Cl_2 solution of **2**·PF_6 + CH_3I. (* = possible isomer of **5**·PF_6)

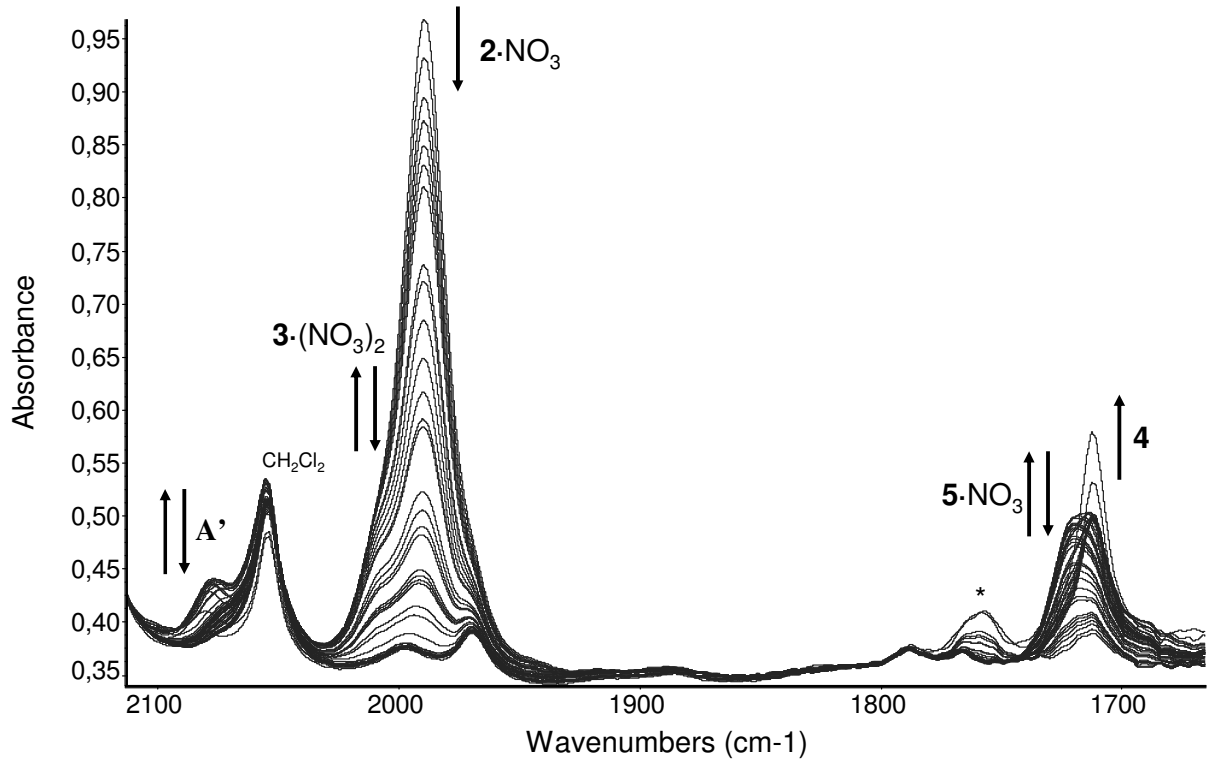

Figure S4. Superimposed FTIR spectra in CH_2Cl_2 solution of **2**·NO_3 + CH_3I. (* = possible isomer of **5**·NO_3)

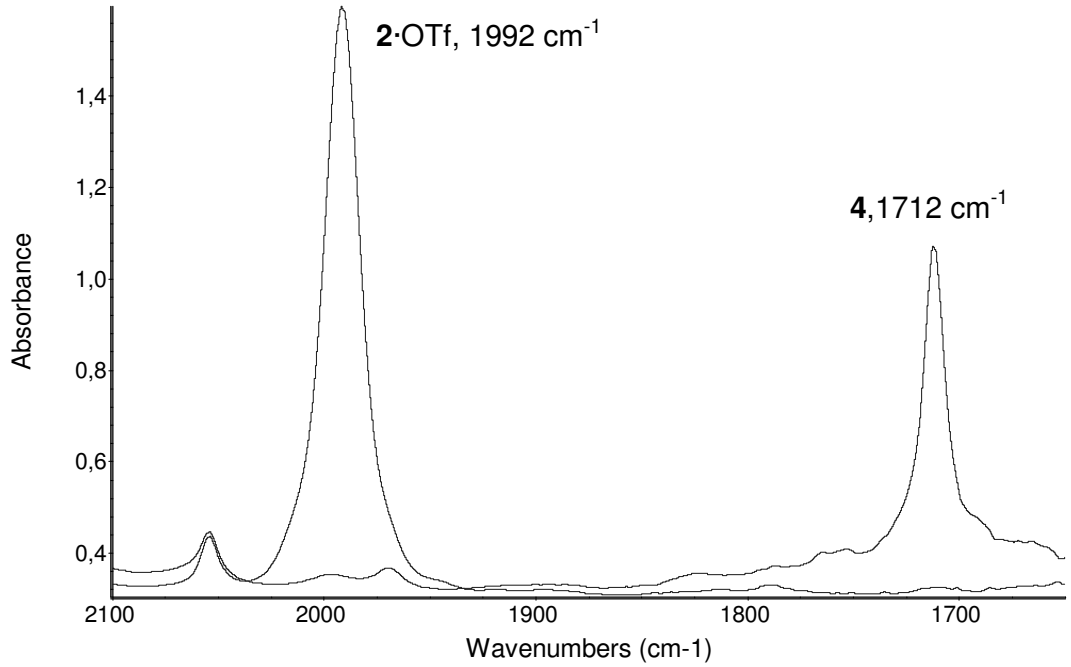

Figure S5. Superimposed FTIR spectra in CH_2Cl_2 solution of **2**·OTf + CH_3I at the beginning (1992 cm^{-1}) and at the end (1712 cm^{-1}) of the reaction.

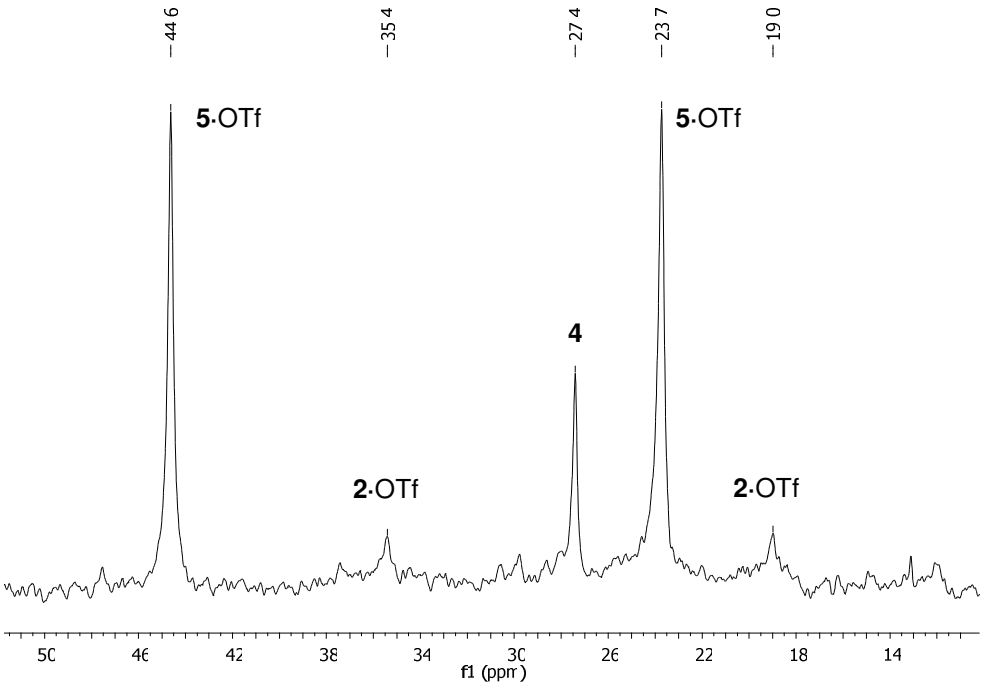

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **2**·OTf + CH_3I in CD_2Cl_2 after 2 hours.

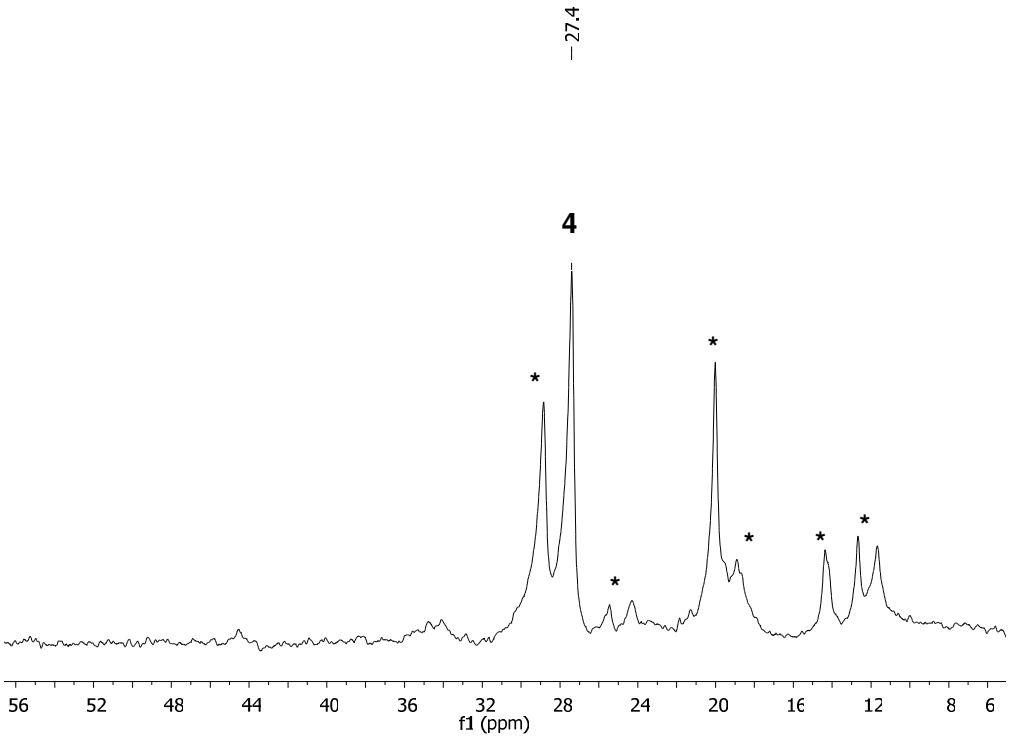

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **2**·OTf + CH_3I in CD_2Cl_2 after 2 days; * corresponds to unidentified decomposition products.

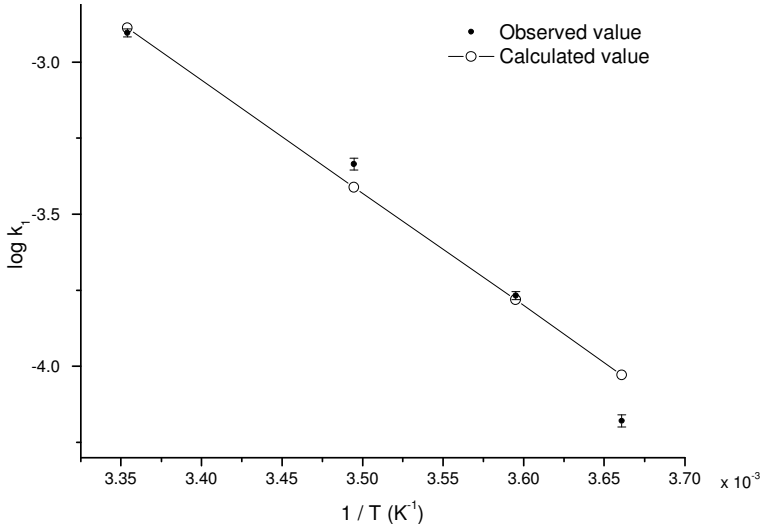

Figure S8. Linearized Eyring plot [log (k_1/T) *vs.* 1/T] for the reaction of **1** with CH_3I

Table S2. Second-order rate constants for the reaction **2**·PF_6 + CH_3I at different temperatures (standard deviations are given in parentheses). The corresponding least-square sample standard deviations (σ) are also reported.

Temperature (K)	k (M^{-1} s^{-1})	σ
280.16	0.64(3) x 10^{-5}	1.02 x 10^{-3}
291.16	1.71(2) x 10^{-5}	3.07 x 10^{-3}
298.16	2.56(6) x 10^{-5}	7.66 x 10^{-3}

[a] $\sigma = [\Sigma_i (I_i^o - I_i^c)^2/(n - m)]^{1/2}$, where I_i^o, I_i^c are the observed and calculated integral values, i is the number of the spectrum, n is the number of observations and m is the number of parameters refined.

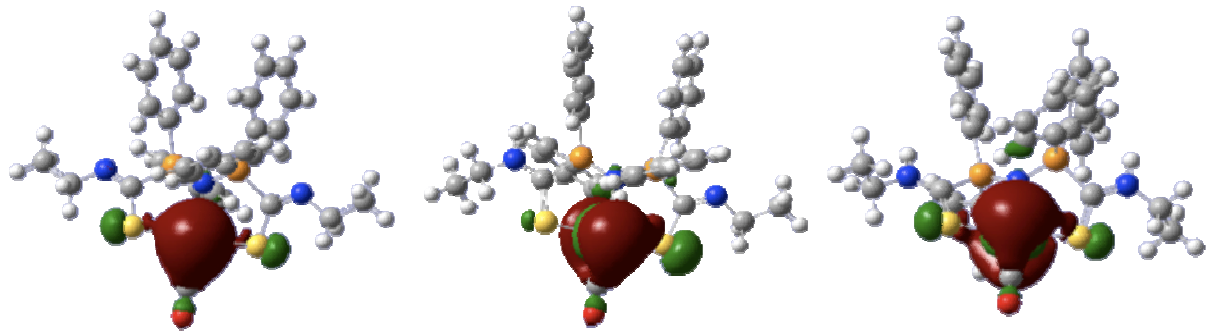

Figure S10. Drawings of the highest energy σ-simmetry MOs for **1**, **2** and **3**.

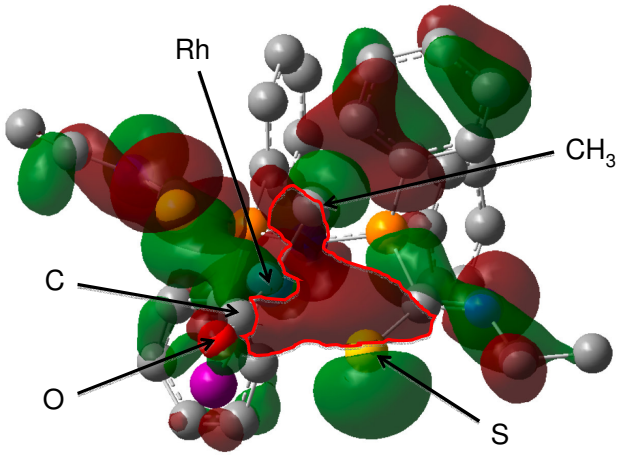

Figure S11. Drawing of the optimized structure of the [(EtSNS)Rh(CO)ICH$_3$] complex (**A**) with continous in-phase MO. The MO involves the CH$_3$ group, the Rh atom, one S atom of the ligand and the C atom of the CO group.